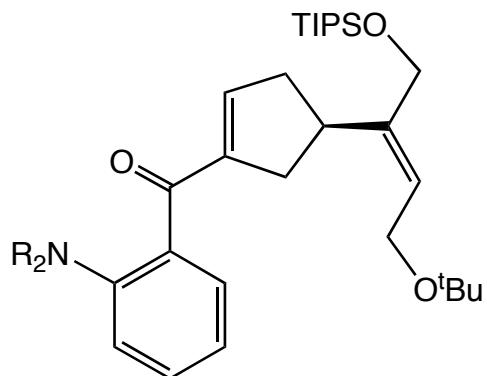
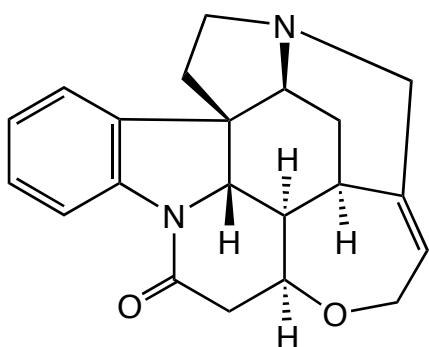


# SYNTHESIS: A COMPARISON

## ORGANIC

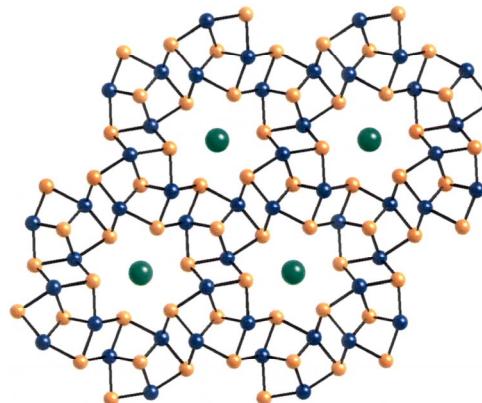


↓  
~12 steps



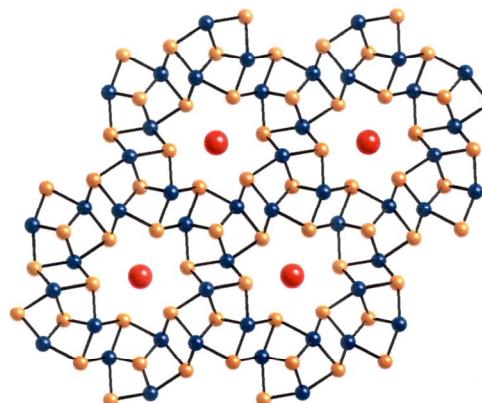
(-)-strychnine

## SOLID STATE



$Tl_{0.4}Nb_3Se_4$

KI ↓ 680 °C



$K_{0.4}Nb_3Se_4$

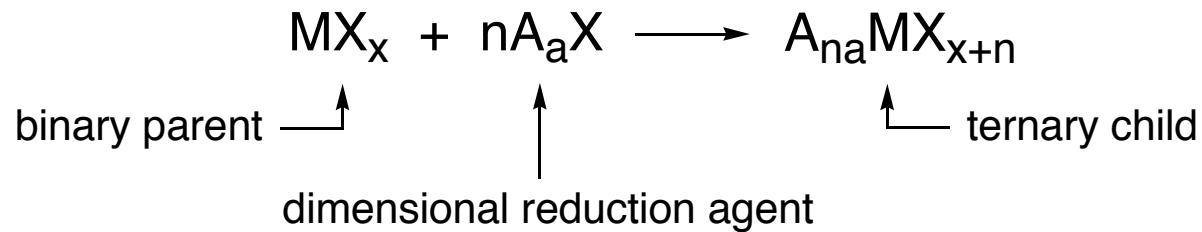
- Hundreds of general reaction types
- Each carefully evaluated for:
  - optimal reaction conditions
  - functional group compatibility

- Five general reaction types:
  - ion exchange, intercalation,
  - topochemical condensation,
  - isomorphous substitution,
  - "crystal engineering"

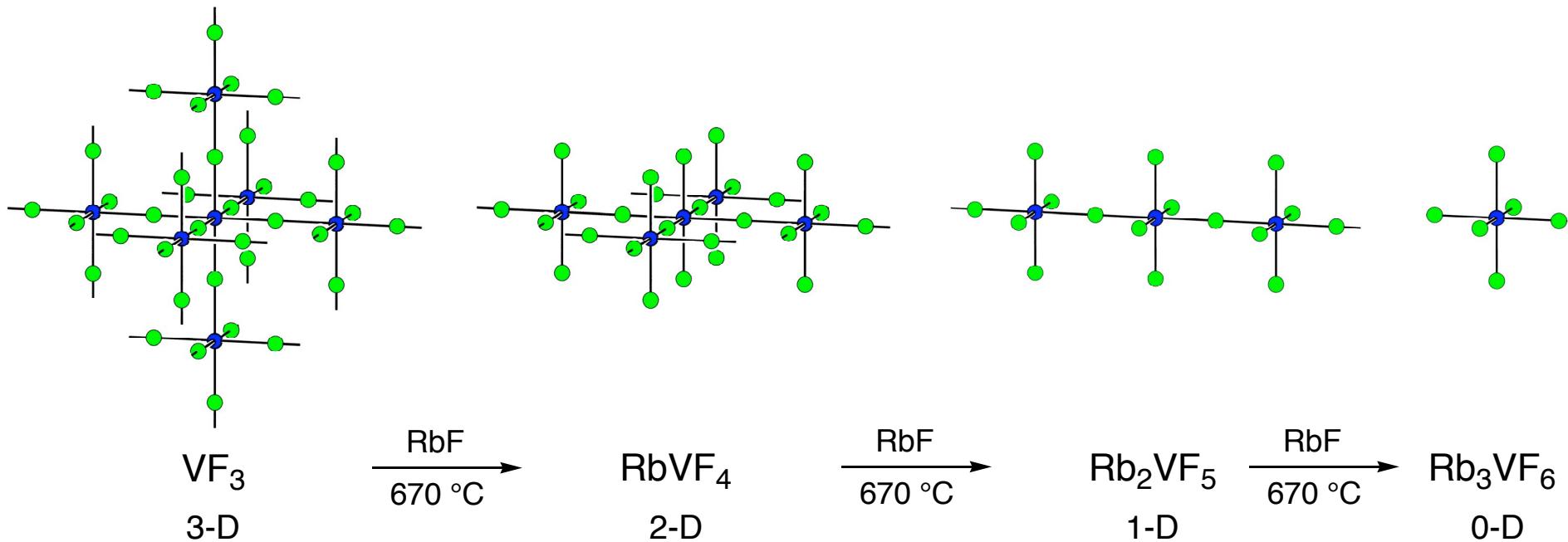
Knight, S. D.; Overman, L. E.; Pairaudeau, G. *J. Am. Chem. Soc.* **1993**, *115*, 9293.

Huan, G.; Greenblatt, M. *Mater. Res. Bull.* **1987**, *22*, 505.

# DIMENSIONAL REDUCTION



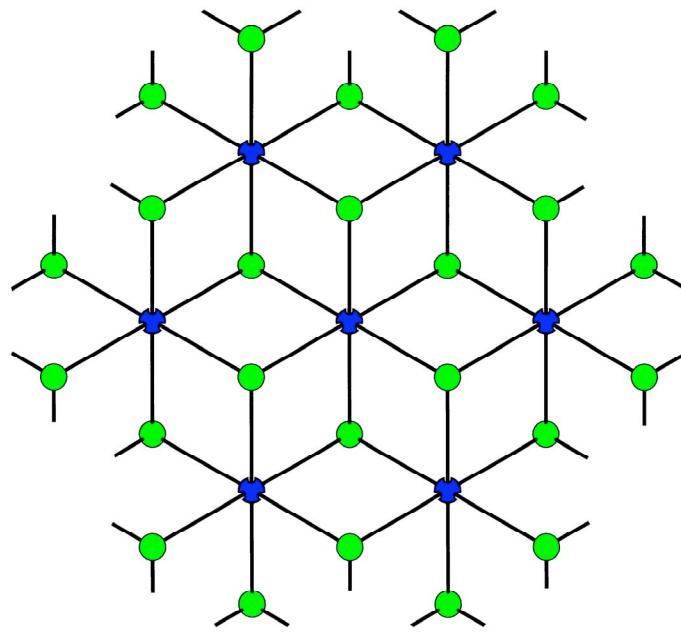
- A general solid state reaction type where a binary parent structure is dismantled by incorporating additional bridge-terminating anions



- Scope and limitations of this predictive reaction scheme have been assessed by examining database of >3000 proven crystal structures: <http://alchemy.ccchem.berkeley.edu/dimred>

# DIMENSIONAL REDUCTION OF O<sub>2</sub>-MX<sub>2</sub>

CdCl<sub>2</sub> structure type:



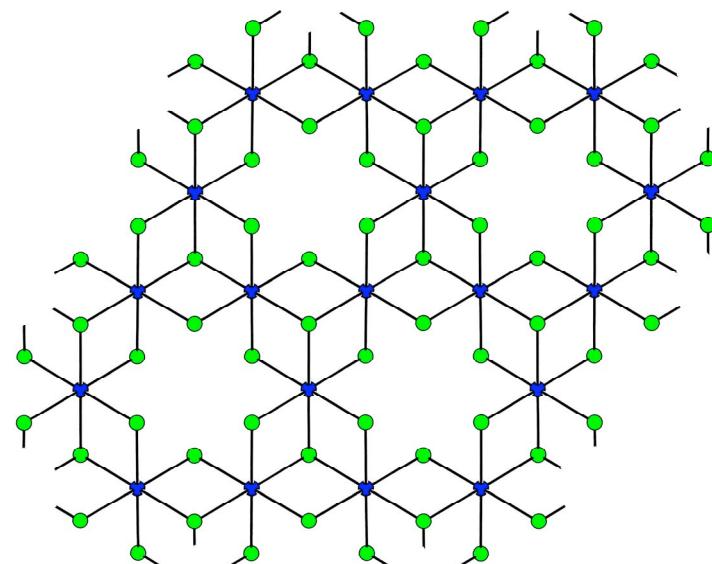
**34% consistent**

Formula	Conn.	Dim.	No.	Examples
MX <sub>2</sub>	12	2-D	50	CdCl <sub>2</sub> , SnS <sub>2</sub>
AM <sub>4</sub> X <sub>9</sub>	11	3-D	1	CsMn <sub>4</sub> Cl <sub>9</sub>
A <sub>2</sub> M <sub>3</sub> X <sub>8</sub>	8	2-D	2	Na <sub>2</sub> Mn <sub>3</sub> Cl <sub>8</sub>
AMX <sub>3</sub>	8	1-D	30	KFeCl <sub>3</sub> , SnZrS <sub>3</sub>
AMX <sub>3</sub>	6	2-D	1	NaMnCl <sub>3</sub>
A <sub>2</sub> MX <sub>4</sub>	4	1-D	8	Na <sub>2</sub> MnCl <sub>4</sub>
A <sub>2</sub> MX <sub>4</sub>	—	—	6	Li <sub>2</sub> FeCl <sub>4</sub>
A <sub>4</sub> M <sub>3</sub> X <sub>12</sub> ·A <sub>2</sub> X <sub>3</sub>	4	1-D	2	La <sub>2</sub> SnS <sub>5</sub>
A <sub>4</sub> MX <sub>6</sub>	0	0-D	24	Tl <sub>4</sub> CrI <sub>6</sub> , Na <sub>6</sub> MnCl <sub>8</sub>

# DIMENSIONAL REDUCTION OF $\text{MnCl}_2$

$\text{MnCl}_2$

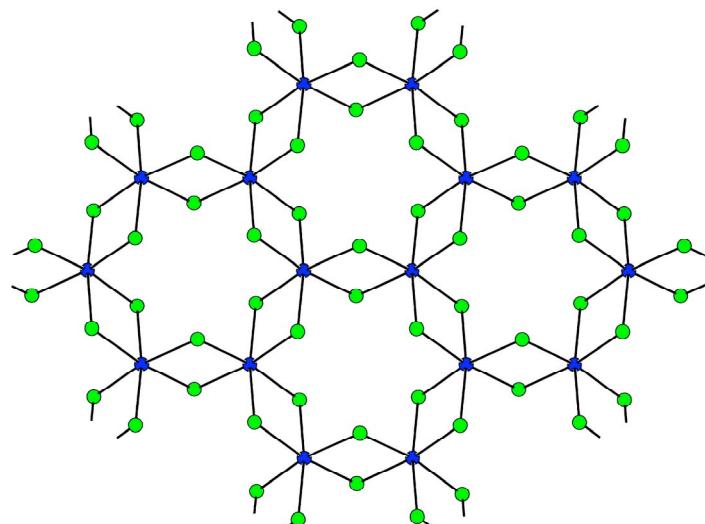
$\downarrow$   
 $^{2/3}\text{NaCl}$



12-connected  
2-D

$\text{Na}_2\text{Mn}_3\text{Cl}_8$

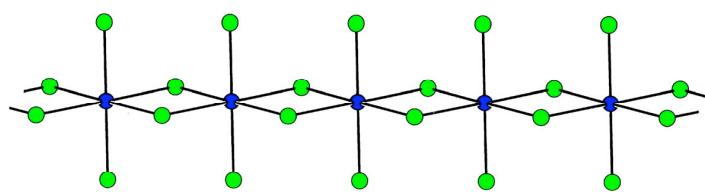
$\downarrow$   
 $^{1/3}\text{NaCl}$



8-connected  
2-D

$\text{NaMnCl}_3$

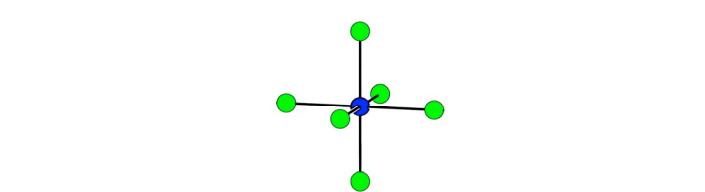
$\downarrow$   
 $\text{NaCl}$



6-connected  
2-D

$\text{Na}_2\text{MnCl}_4$

$\downarrow$   
 $2\text{NaCl}$



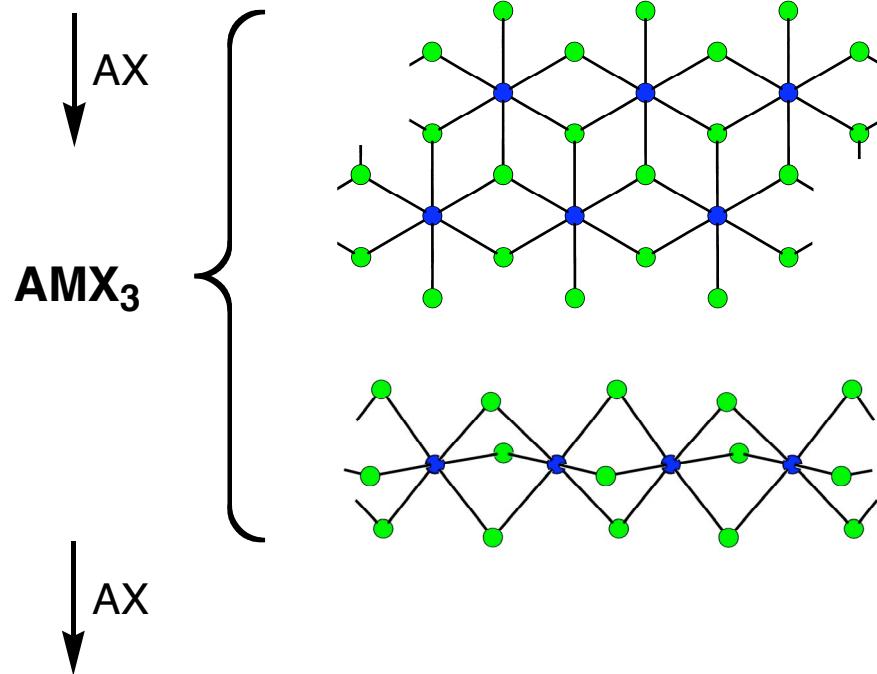
4-connected  
1-D

$\text{Na}_4\text{MnCl}_6$

0-connected  
0-D

# INFLUENCE OF COUNTERCATION A

$O_2\text{-MX}_2$



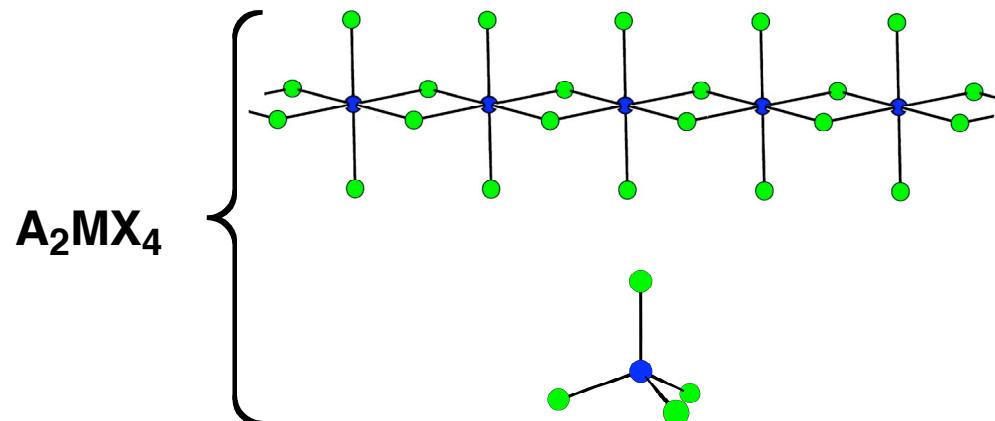
A

---

Li Na In K Tl Rb Cs

1 1 3 6 7 3 1

0 0 0 1 5 11 18

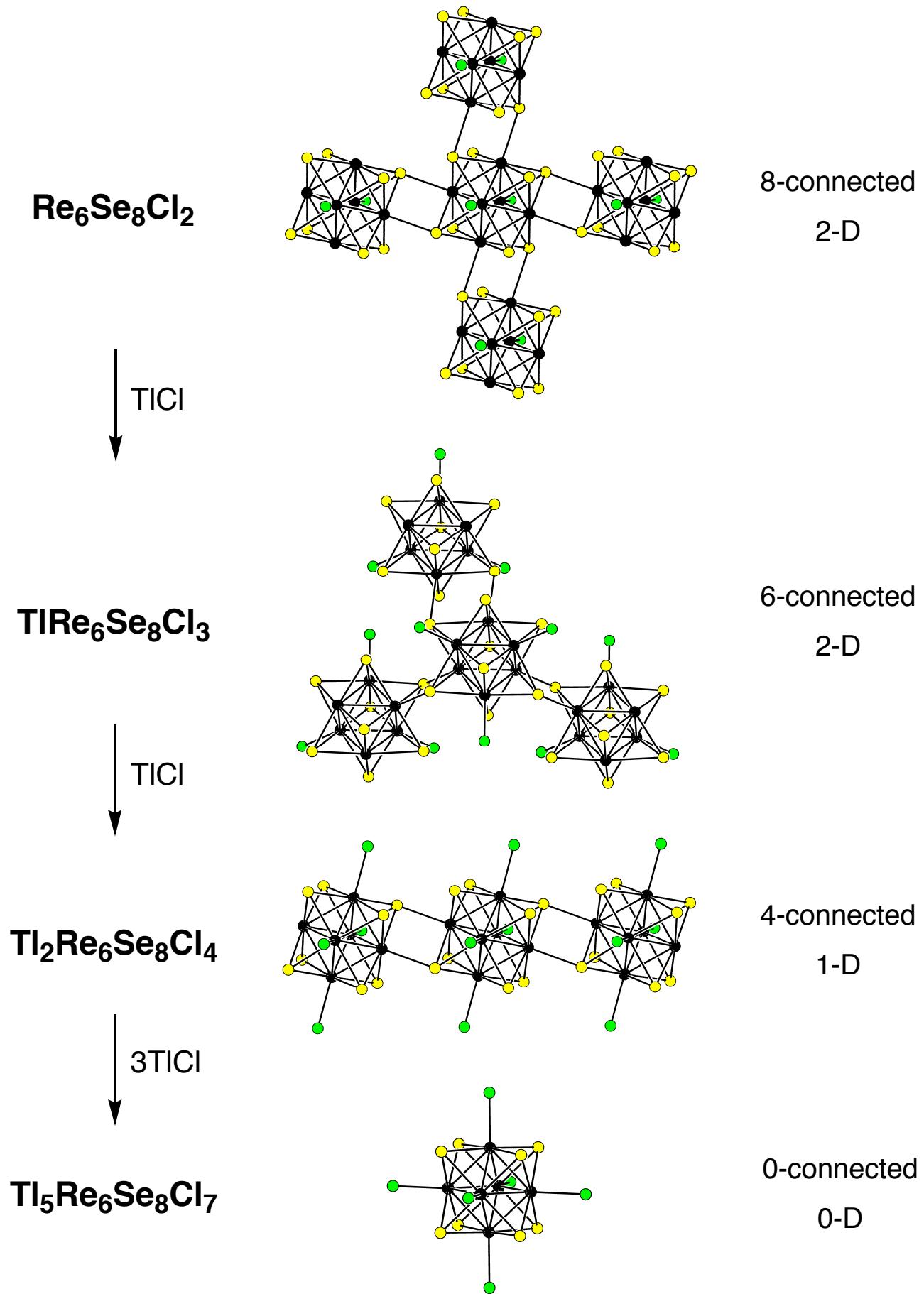


7 3 0 0 0 0 0

3 3 0 4 0 6 11

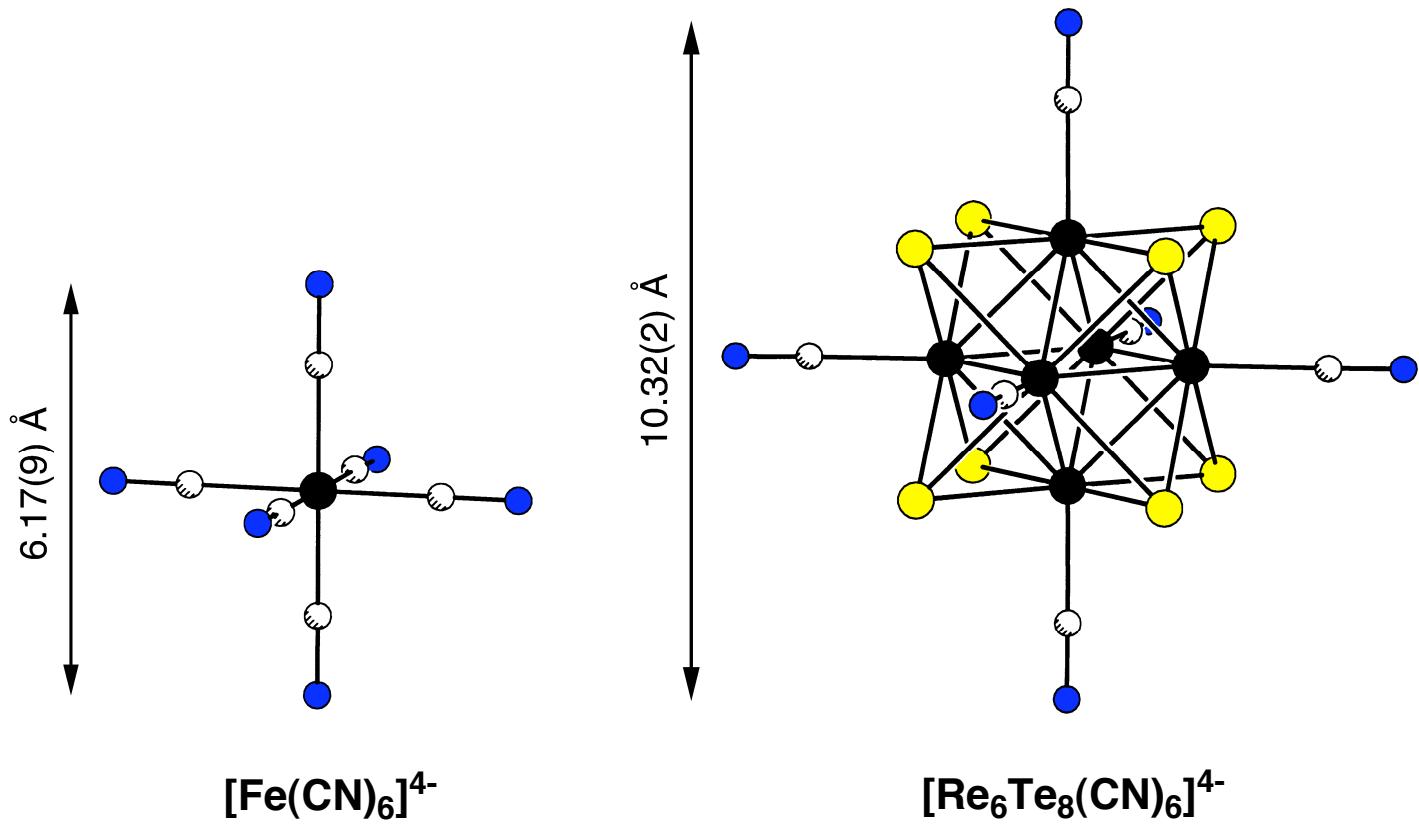
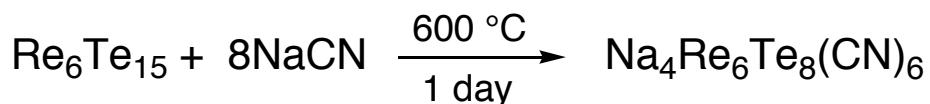
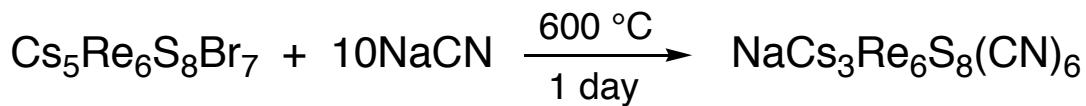
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# DIMENSIONAL REDUCTION OF $\text{Re}_6\text{Se}_8\text{Cl}_2$



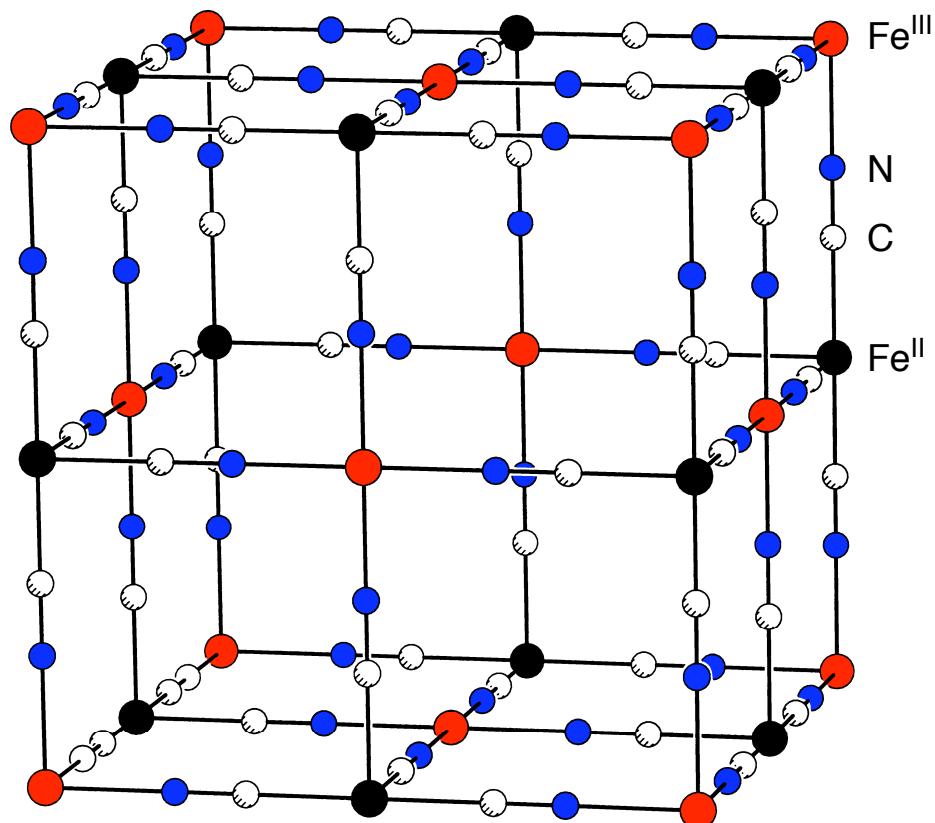
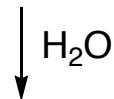
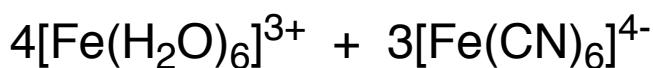
# ENLARGED CYANOMETALATES:

## $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ )



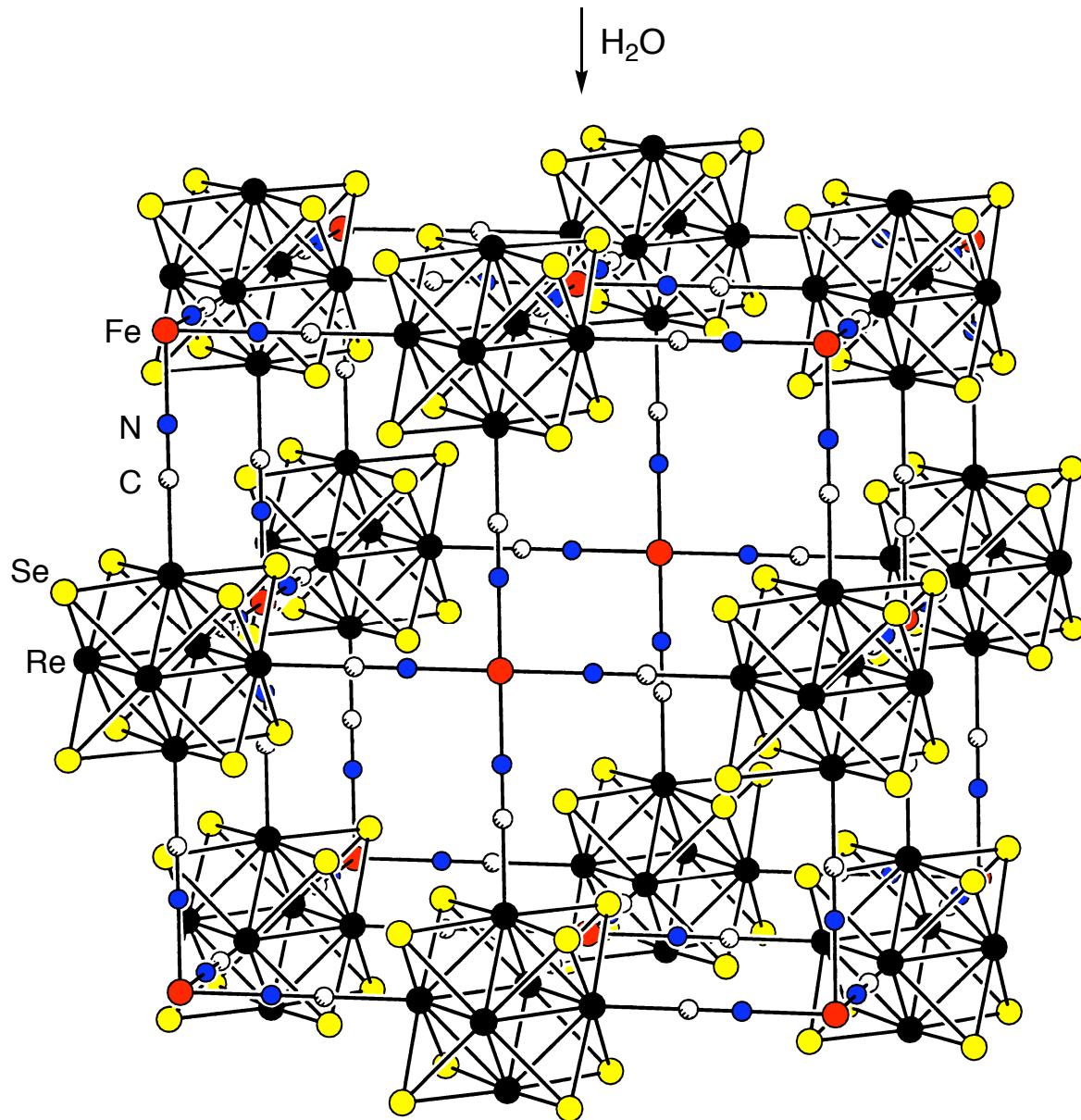
Mironov, Y. V.; Cody, J. A.; Albrecht-Schmitt, T. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 493.  
 Beauvais, L. G.; Shores, M. P.; Long, J. R. *Chem. Mater.* **1998**, *10*, 3783.

# PRUSSIAN BLUE



- One quarter of the  $[\text{Fe}(\text{CN})_6]^{4-}$  units are missing from the structure
- These vacancies give rise to cavities with a volume of  $557 \text{ \AA}^3$
- Dehydration generates coordinatively unsaturated  $\text{Fe}^{\text{III}}$  sites

# CLUSTER-EXPANDED PRUSSIAN BLUE



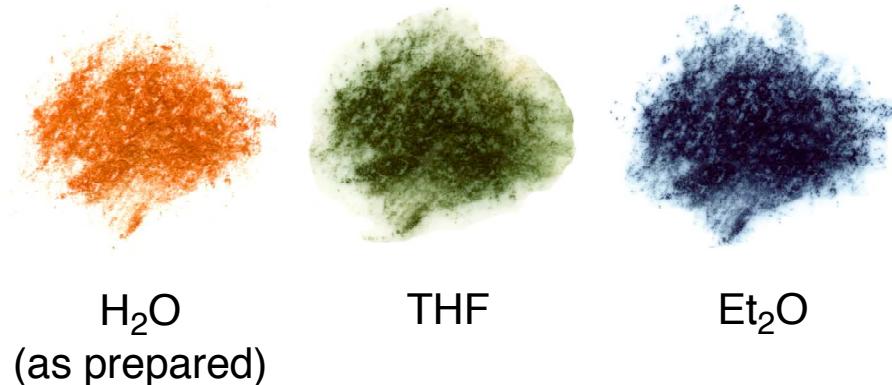
- One quarter of the  $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$  units are missing from the structure
- These vacancies give rise to cavities with a volume of  $1579 \text{ \AA}^3$
- Dehydration generates coordinatively unsaturated  $\text{Fe}^{\text{III}}$  sites

# CLUSTER-EXPANDED METAL-CYANIDE FRAMEWORKS

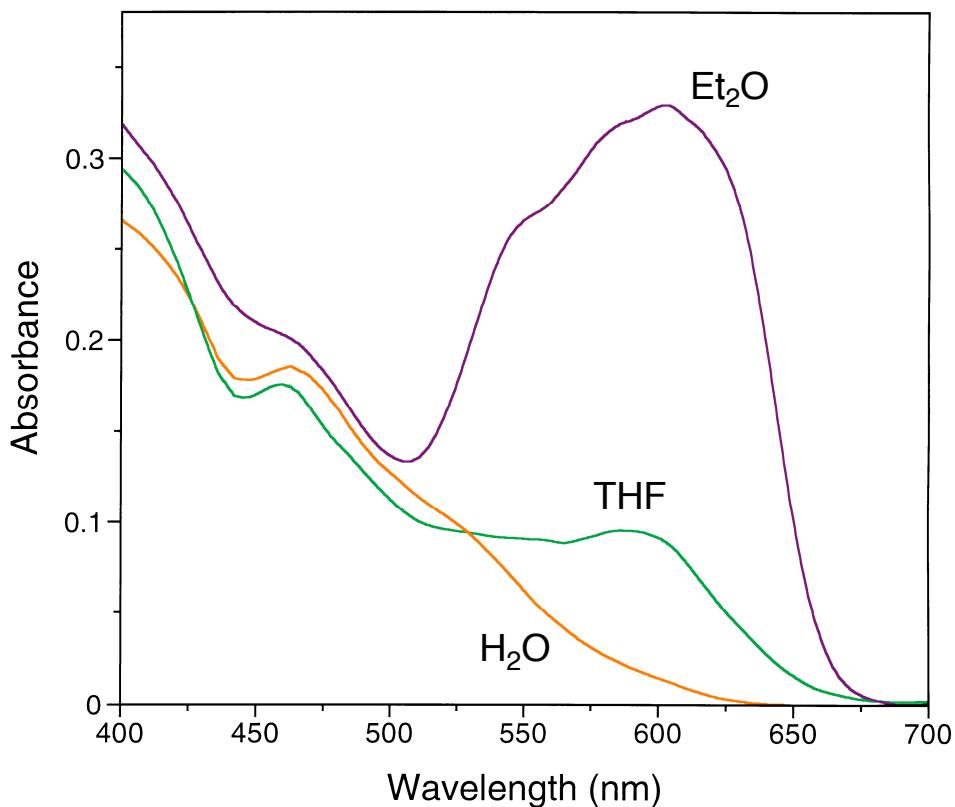
known structure types	cluster-expanded analogue	dim.
$\text{Ga}[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$	$\text{Ga}[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 6\text{H}_2\text{O}$	3-D
$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$	$\text{Fe}_4[\text{Re}_6\text{Se}_8(\text{CN})_6]_3 \cdot 36\text{H}_2\text{O}$	3-D
$\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$	$\text{Ni}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 34\text{H}_2\text{O}$	3-D
$[\text{Mn}_2(\text{H}_2\text{O})_4][\text{Ru}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$	$[\text{Co}_2(\text{H}_2\text{O})_4][\text{Re}_6\text{S}_8(\text{CN})_6] \cdot 5\text{H}_2\text{O}$	3-D
$\text{Na}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 \cdot 9\text{H}_2\text{O}$	$\text{Na}_2\text{Zn}_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 24\text{H}_2\text{O}$	3-D
$\text{La}[\text{Co}(\text{CN})_6] \cdot 18\text{H}_2\text{O}$		3-D
$\text{Sm}[\text{Co}(\text{CN})_6] \cdot 18\text{H}_2\text{O}$		3-D
$\text{Ba}_3[\text{Cr}(\text{CN})_6]_2 \cdot 20\text{H}_2\text{O}$	$\text{Cs}_2[\text{Fe}(\text{H}_2\text{O})_2]_3[\text{Re}_6\text{Se}_8(\text{CN})_6]_2 \cdot 12\text{H}_2\text{O}$	3-D
$[\text{Zn}(\text{H}_2\text{O})]_2[\text{Fe}(\text{CN})_6] \cdot 0.5\text{H}_2\text{O}$	$[\text{Zn}(\text{H}_2\text{O})]_2[\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot 13\text{H}_2\text{O}$	2-D
$\text{Na}_2[\text{Cu}(\text{H}_2\text{O})_2][\text{Fe}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$	$\text{Cs}_2[\text{Mn}(\text{H}_2\text{O})_2][\text{Re}_6\text{S}_8(\text{CN})_6]$	2-D
$(\text{NMe}_4)_2\text{Mn}[\text{Mn}(\text{H}_2\text{O})_2][\text{Cr}(\text{CN})_6]_2 \cdot 2\text{H}_2\text{O}$		2-D
$(\text{NMe}_4)[\text{Mn}(\text{H}_2\text{O})_4][\text{Fe}(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$	$(\text{NPr}_4)[\text{Mn}(\text{H}_2\text{O})_4][\text{Re}_6\text{S}_8(\text{CN})_6]_2 \cdot 4\text{H}_2\text{O}$	1-D

# SOLVENT-INDUCED COLOR CHANGES

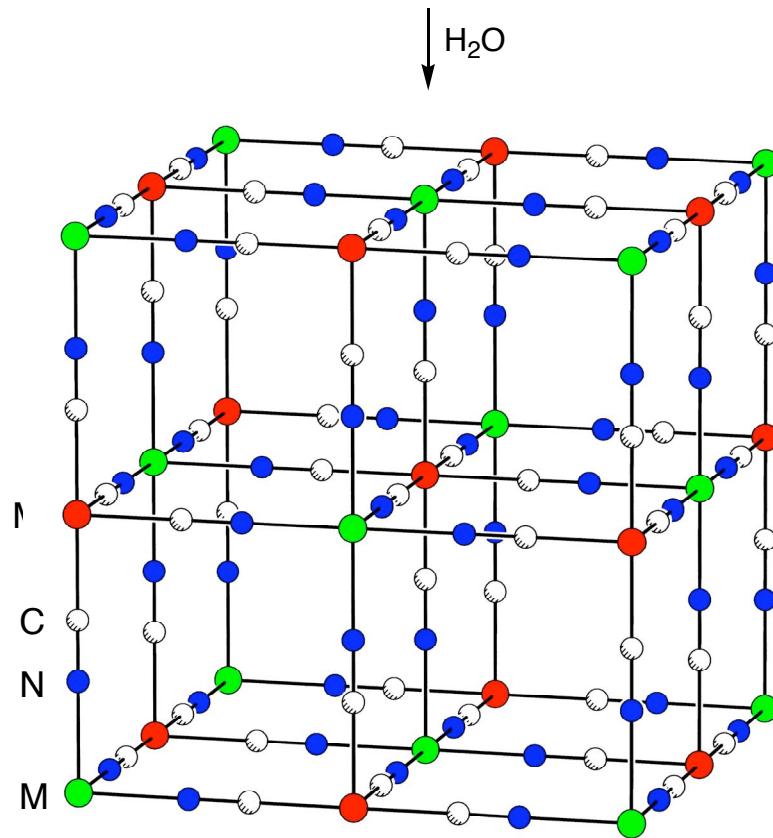
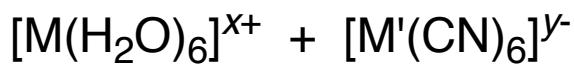
- Solid  $[\text{Co}_2(\text{H}_2\text{O})_4][\text{Co}(\text{H}_2\text{O})_3]_4[\text{Re}_6\text{Se}_8(\text{CN})_6]_3 \cdot 43\text{H}_2\text{O}$  rapidly and reversibly changes color upon exposure to certain solvent vapors:



- Color changes are associated with new absorption features in the 550-650 nm region, and are readily quantified from the diffuse reflectance uv-vis spectra:



# MAGNETIC PRUSSIAN BLUE ANALOGUES



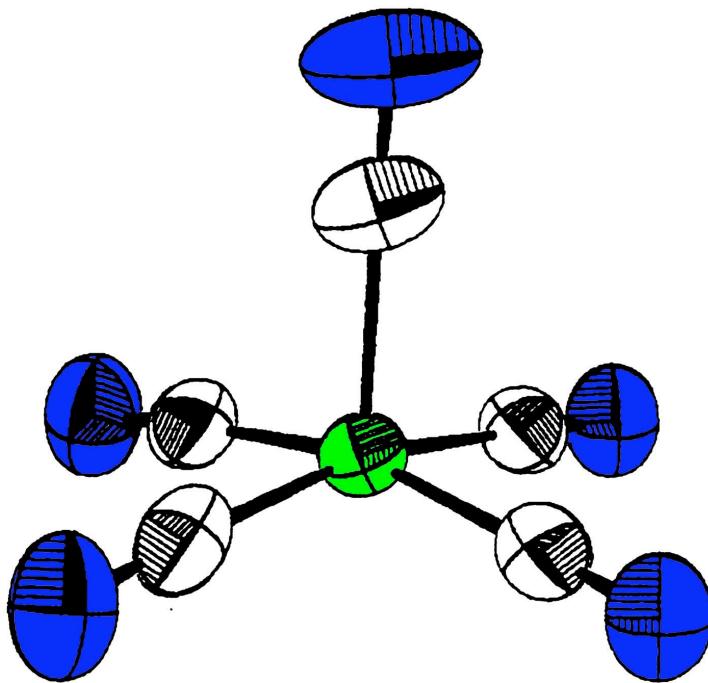
compound	coupling*	ordering T (K)
$Mn^{II}[Mn^{IV}(CN)_6]\cdot zH_2O$	AF	49
$CsNi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$	F	90
$Cs_2Mn^{II}[V^{II}(CN)_6]$	AF	125
$(Et_4N)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$	AF	230
$Cr^{II}_3[Cr^{III}(CN)_6]_2\cdot 10H_2O$	AF	240
$V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86}\cdot 2.8H_2O$	AF	315
$KV^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$	AF	376

\*F = ferromagnetic, AF = antiferromagnetic

Mallah, T.; Thiébaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554.

Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397.

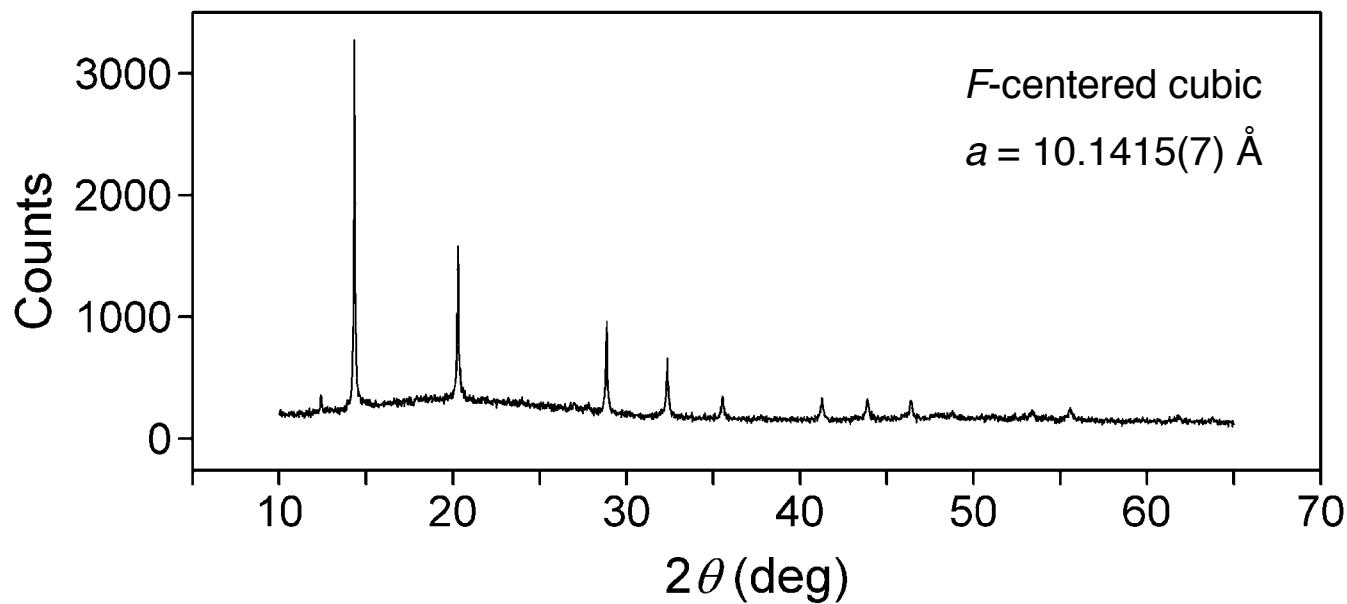
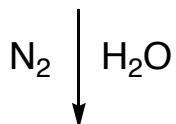
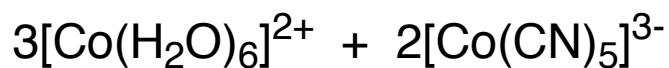
# COBALT PENTACYANIDE



- As crystallized in (NEt<sub>2</sub>)<sup>i</sup>Pr<sub>2</sub>)<sub>3</sub>[Co(CN)<sub>5</sub>]<sup>\*</sup>
- Geometry is square pyramidal with C<sub>apical</sub>-Co-C<sub>basal</sub> = 97.6(8)<sup>°</sup>
- Low-spin cobalt(II) complex with S = 1/2

\*Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, 14, 2590

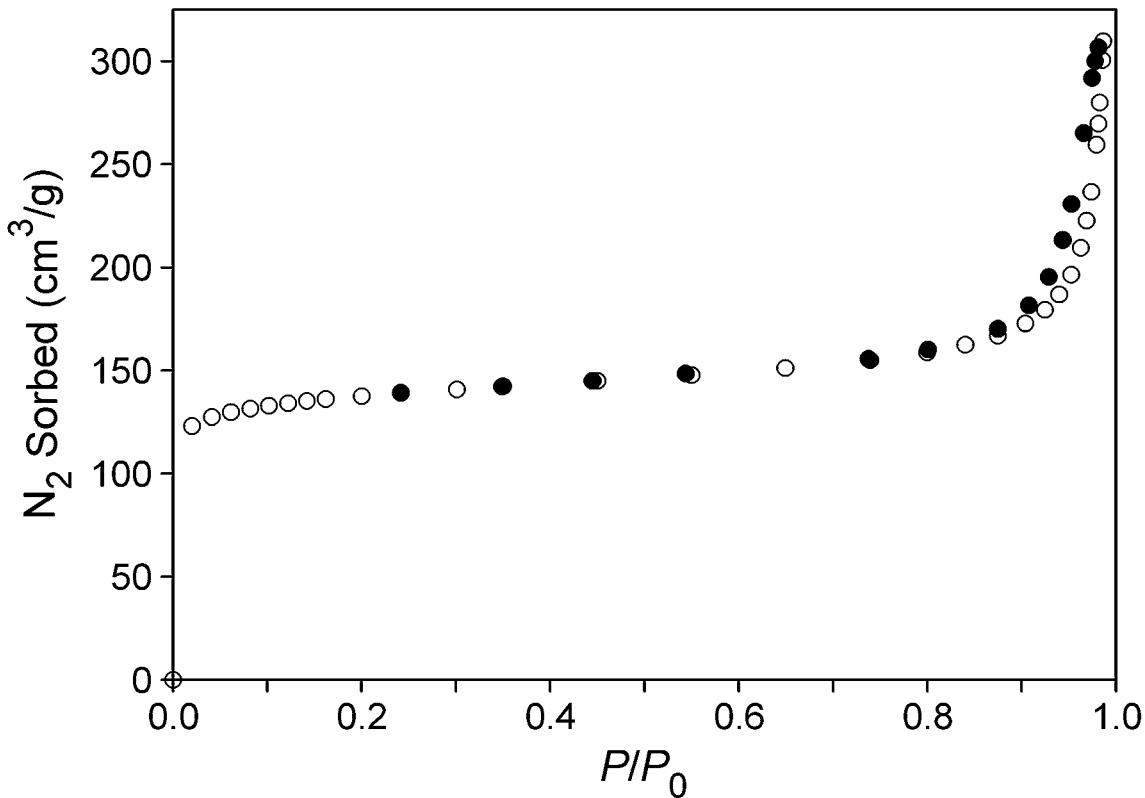
# A NEW PRUSSIAN BLUE ANALOGUE



- X-ray powder diffraction indicates cubic Prussian blue type structure
- Vacancies at  $\frac{1}{3}$  of cyanometalate sites and  $\frac{1}{6}$  of remaining  $\text{CN}^-$  sites

# N<sub>2</sub> SORPTION

- Co<sub>3</sub>[Co(CN)<sub>5</sub>]<sub>2</sub> retains crystallinity upon dehydration at 100 °C



- Type I sorption isotherm characteristic of a microporous solid
- Sorption capacity at 77 K and 700 torr of N<sub>2</sub> is comparable to that of dehydrated zeolites:

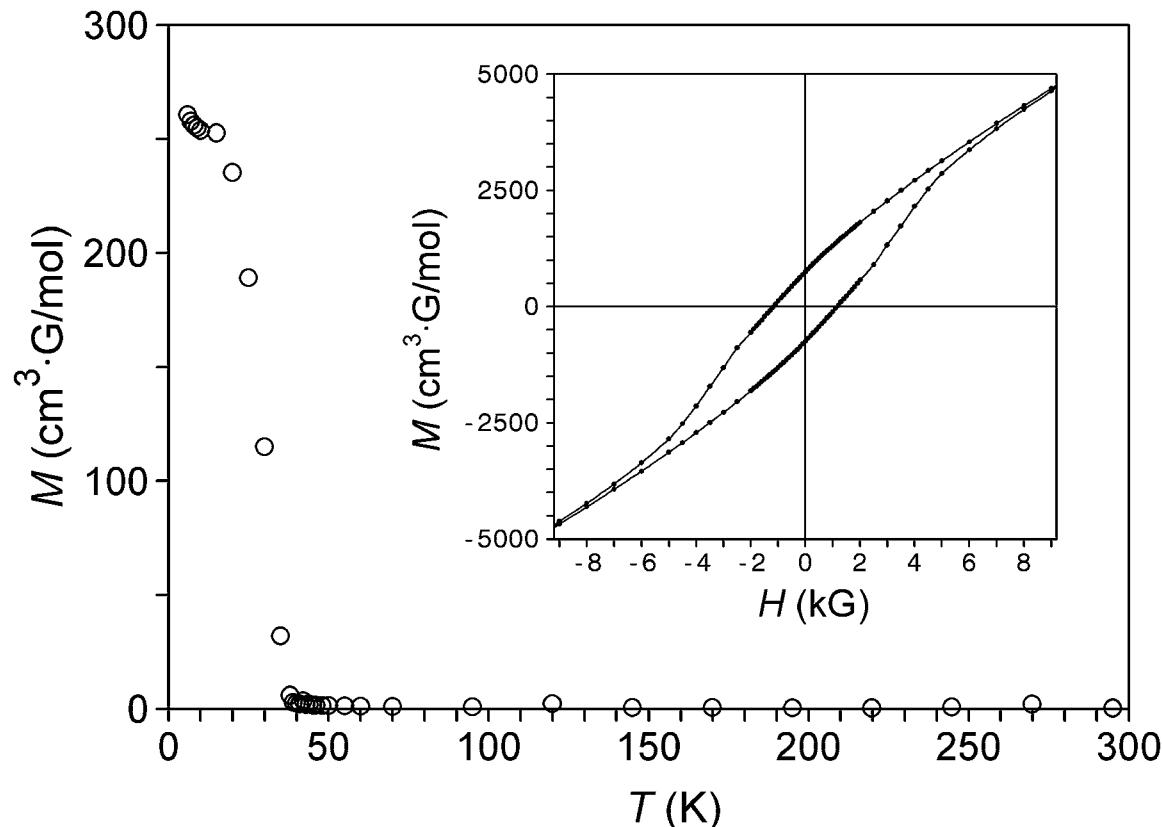
Co <sub>3</sub> [Co(CN) <sub>5</sub> ] <sub>2</sub>	179 cm <sup>3</sup> /g
erdionite	155 cm <sup>3</sup> /g
faujasite	192 cm <sup>3</sup> /g

Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, 124, 12096

Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1974, pp. 607-627

# A MICROPOROUS MAGNET

- Dehydrated  $\text{Co}_3[\text{Co}(\text{CN})_5]_2$  displays magnetic ordering below 38 K:



- Minimum in  $\square_M T$  at 75 K and Weiss constant of  $\square = -31$  K indicate ferrimagnetic behavior
- Coercive field of 1160 G at 5 K is the largest yet observed for a Prussian blue analogue